Research Article

Effect of Stepwise Replacement of Non-Oxide to Oxide Group on Structural Properties of Bi$_2$O$_3$·LiF·B$_2$O$_3$ Glasses

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Bismuth fluoroborate glasses with compositions $x$Bi$_2$O$_3$·$(40 - x)$LiF·60B$_2$O$_3$ ($x = 0, 5, 10, 15,$ and $20$) are synthesized by melt-quench method. XRD pattern is obtained for all the samples to confirm their amorphous nature. FTIR spectroscopy is carried out for the reported samples. It reflects the effect of replacement of a non-oxide group (LiF) with an oxide group (Bi$_2$O$_3$) in the glass network, due to the presence of the various absorption bands and their shifting with such replacement, assigning a role of network modifier to Bi$_2$O$_3$. Density and molar volume show an increase in their values with increase in Bi$_2$O$_3$ concentration. Theoretical optical basicity is calculated for the reported samples, which shows a decreasing trend with the increasing concentration of Bi$_2$O$_3$.

1. Introduction

Bi$_2$O$_3$ is one of the best glass formers due to the sheet-like structure of boron-oxygen triangles in borate glasses, with their ability to connect themselves to form a network [1, 2]. A random arrangement of various atomic and molecular species is easily formed in borate glasses which is the basic requirement for glass formation. A number of modifications in the properties of the borate glasses, with the addition of alkali halides, have been reported so far [3–9]. The inclusion of LiF in the borate glass network brings out some structural changes [3], which in turn become responsible for the change in various properties. Some new units like BO$_2$F, BO$_2$F$_2$, BOF$_3$, and BO$_3$F are formed by the replacement of few oxygen atoms by fluorine ions [4–6]. Also, there may be an increase in the number of polyhedral groups of boron and oxygen, which in turn increases the number of nonbridging oxygen atoms [7–9].

Bi$_2$O$_3$ possesses high third-order nonlinear optical susceptibility caused by high density and refractive index [10, 11]. This property makes it to have numerous nonlinearity applications such as optical switching [12, 13], supercontinuum generation [14], and wavelength conversion [15]. Luminescent materials have always been studied by researchers for their wide range of applications. Noto reported the luminescence spectroscopy of some systems containing rare earth ions [16, 17]. Also, bismuth ion acts as an efficient luminescent activator with applications in lasers as a sensitizer for some rare earth ions [18, 19]. The purpose of this paper is to report the change in structural and physical properties of LiF-B$_2$O$_3$ glasses with the stepwise replacement of LiF by Bi$_2$O$_3$. The addition of Bi$_2$O$_3$ provides an opportunity for the new molecular units to be formed with more numbers of NBOs.

2. Experimental Details

Bi$_2$O$_3$ containing fluoroborate glasses with compositions $x$Bi$_2$O$_3$·$(40 - x)$LiF·60B$_2$O$_3$ ($x = 0, 5, 10, 15,$ and $20$) were synthesized through melt-quench method using Bi$_2$O$_3$, LiF and H$_3$BO$_3$, reagent grade powders. A uniform mixture of the various powdered samples was prepared and heated at 1273 K for 30 minutes. The bubble free melt so formed was pressed between two carbon plates at room temperature. The glassy samples were thus obtained in the form of thin pallets.

The samples were tested for their amorphous nature on Rigaku X-ray diffractometer using Cu-Kα radiations. The samples ground to powdered form were placed in the diffractometer and rotated at 1°/min.
FTIR spectroscopy was carried out at room temperature in the range from 652 to 4000 cm\(^{-1}\). The samples were exposed to the IR radiations in Perkin-Elmer FTIR spectrophotometer. A plot between % transmission and wave number is obtained to examine various bonds formation in view of absorption bands obtained in the plot. Densities \((d)\) of the samples were calculated at room temperature using Archimedes’ principle with xylene was taken as an inert immersion liquid.

3. Results and Discussion

3.1. XRD Analysis. The X-ray diffraction pattern for \(x\)Bi\(_2\)O\(_3\) \(·\) \((40 − x)\)LiF \(·\) 60B\(_2\)O\(_3\) glasses with \(x = 0, 5, 10, 15\) and 20 is plotted in Figure 1. The patterns contain broad bands but do not contain any peak, which confirms the amorphous nature of the samples.

3.2. FTIR Analysis. Figure 2 corresponds to the Fourier transform infrared spectra of the compositions \(x\)Bi\(_2\)O\(_3\) \(·\) \((40 − x)\) − 60B\(_2\)O\(_3\), with \(x = 0, 5, 10, 15, \) and 20. The spectra were recorded in the range, 652–4000 cm\(^{-1}\). However, absorption bands obtained in the range of 1700–4000 cm\(^{-1}\) correspond to those due to water groups, the said range is not shown in the figure.

In the composition with \(x = 0\), there appears an absorption band around 685 cm\(^{-1}\). This absorption is attributed to the bending of B–O–B linkage in the borate network [20]. However for the compositions with \(x = 5, 10, 15, \) and 20, in general, this absorption becomes very weak which reveals that the structural changes are taking place due to the addition of Bi\(_2\)O\(_3\). For all the samples, there appears an absorption band with small but increasing intensity, around 779 cm\(^{-1}\). This absorption is due to the formation of B–F bonds [21]. This indicates that due to addition of Bi\(_2\)O\(_3\), structure of the glass is greatly affected as fluorine gets encouraged to take interstitial positions in the glass network.

In the composition with \(x = 0\), the absorption band around 910 cm\(^{-1}\) is attributed to the B–O bond stretching in BO\(_4\) units of diborate groups [22]. In the compositions except \(x = 0\), there appears another band originating at 901 cm\(^{-1}\). Intensity of this band increases with increase in Bi\(_2\)O\(_3\) concentration. It may be due to the Bi–O and Bi–O–Bi bonds in BiO\(_6\) octahedra [20, 21, 23–25].

For the samples with \(x = 5, 10, 15 \) and 20, inclusion of Bi\(_2\)O\(_3\) in the host composition facilitates the presence of more oxygen atoms in the glass network. The availability of these oxygen atoms encourages the formation of more pentaborate and diborate species [26, 27] in the glass network. Presence of these species is attested by the increasing intensity band in \(x = 5, 10, 15\), and 20 at 1100 cm\(^{-1}\), which is almost absent in \(x = 0\).

In the literature [22, 26, 28], the absorption range 1160–1600 cm\(^{-1}\) is assigned to the B–O bond stretching vibrations in BO\(_3\) units. Here one can observe two sub-bands in all the compositions. For \(x = 0\), the sub-bands are centered at 1220 cm\(^{-1}\) and 1365 cm\(^{-1}\). The former band corresponds to the stretching vibrations of B–O bonds in BO\(_3\) units from meta and ortho-borate groups [21, 22, 25–28] and the later is due to the B–O asymmetric stretching vibrations in BO\(_3\) and BO\(_3^-\) units [22, 25, 26]. For the compositions other than \(x = 0\), these sub-bands appear at 1210 cm\(^{-1}\) and 1370 cm\(^{-1}\) respectively, with an enhanced intensity. The enhancement in the intensity of the band centered at 1210 cm\(^{-1}\) may be due to the formation of more BO\(_3\) units in meta and ortho borate groups with the addition of oxygen containing Bi\(_2\)O\(_3\) molecule in the glass network. The increasing intensity of the band centered at 1370 cm\(^{-1}\) is due to the presence of BiO\(_-\) units in the samples other than that with \(x = 0\) [23]. In addition to these two high-intensity bands, there exists a shoulder absorption at 1295 cm\(^{-1}\) for the samples with Bi\(_2\)O\(_3\) concentration. This shoulder absorption is assigned to the BO\(_2\)F units [29] and also may be due to Bi–O–Bi vibrations of BiO\(_6\) octahedral units [23]. Furthermore the absorption band centered at 1440 cm\(^{-1}\) and 1530 cm\(^{-1}\) in all the samples except \(x = 0\), is due to BO\(_3^-\) stretching vibrations of BO\(_3\) units from varied types of borate groups [30].

All these results are summarized in Table 1.

3.3. Density and Molar Volume. Using Archimedes principle, density \((D)\) of all the samples was calculated, and its values are plotted against Bi\(_2\)O\(_3\) mol% in Figure 3. It is observed that density of the samples increases with increasing concentration of Bi\(_2\)O\(_3\). This shows that the atomic and molecular species get more closely packed with the addition of Bi\(_2\)O\(_3\). The increase of the density of the glasses with the addition of Bi\(_2\)O\(_3\) is probably attributable to a change in cross-link density and coordination numbers of Bi\(_{3+}\) ions [30]. It is supported by another fact that Bi\(_2\)O\(_3\) has larger molar mass as compared to LiF, so the replacement of LiF by Bi\(_2\)O\(_3\) makes the density to increase.

The molar volume \((V_M)\) of each glass sample was calculated using the formula [31]

\[
V_M = \sum x_i M_i / d,
\]

where \(x_i\) is the molar fraction and \(M_i\) is the molecular weight of the \(i\)th component. It also increases with the increase in Bi\(_2\)O\(_3\) content.

3.4. Theoretical Optical Basicity. Optical basicity is an important parameter related to the optical properties of the glasses. Electronic polarizability and optical basicity have an intrinsic relationship. Optical basicity is expressed in terms of the electron density carried by anions. Theoretical optical basicity for the present series of samples is calculated using following formula [32]:

\[
\Lambda_{th} = \sum \frac{(Z_i r_i)}{(Z_i'/y_i)}.
\]

Here \(r_i\) is the ratio of number of cations “\(i\)” to total number of oxide ions, \(y_i\) is basicity modulating factor, \(Z_i\) is the oxidation number of cations “\(i\)” and \(Z_i'\) is the oxidation number of corresponding anions. The basicity
Figure 1: XRD plots for samples with \(x = 0, 5, 10, 15, \text{ and } 20\) in the compositions \(xBi_2O_3 \cdot (40 - x)LiF \cdot 60B_2O_3\). 

Figure 2: FTIR plots for samples with \(x = 0, 5, 10, 15, \text{ and } 20\) in the compositions \(xBi_2O_3 \cdot (40 - x)LiF \cdot 60B_2O_3\). 

The moderating parameter \(\gamma_i\) can be calculated from the following equation:

\[
\gamma_i = 1.36(x_i - 0.26), \tag{3}
\]

where \(x_i\) is Pauling’s, electronegativity of the cation. Values of \(\Lambda_{th}\) are plotted in Figure 4. It is observed that theoretical optical basicity decreases with increase in \(Bi_2O_3\) content.

Table 1: FTIR absorption assignments of the samples with \(x = 0, 5, 10, 15, \text{ and } 20\) in the compositions \(xBi_2O_3 \cdot (40 - x)LiF \cdot 60B_2O_3\).

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>685</td>
<td>Bending of B–O–B linkage in borate network</td>
</tr>
<tr>
<td>779</td>
<td>B–F bonds</td>
</tr>
<tr>
<td>901</td>
<td>Bi–O and Bi–O–Bi bands in BiO(_6) octahedra</td>
</tr>
<tr>
<td>910</td>
<td>B–O bond stretching in BO(_4) units</td>
</tr>
<tr>
<td>1100</td>
<td>Pentaborate and diborate species</td>
</tr>
<tr>
<td>1210, 1220</td>
<td>Stretching vibrations of B–O bonds in BO(_3) units from meta and orthoborate groups</td>
</tr>
<tr>
<td>1295</td>
<td>BO(_2)F units and Bi–O–Bi vibrations of BiO(_6) octahedral units</td>
</tr>
<tr>
<td>1365</td>
<td>B–O asymmetric stretching vibrations in BO(_3) and BO(_3^+) units</td>
</tr>
<tr>
<td>1370</td>
<td>BiO units</td>
</tr>
<tr>
<td>1440, 1530</td>
<td>B–O stretching vibrations of BO(_3) units from varied types of borate groups</td>
</tr>
</tbody>
</table>

Figure 3: Density and Molar Volume of the samples with \(x = 0, 5, 10, 15, \text{ and } 20\) in the compositions \(xBi_2O_3 \cdot (40 - x)LiF \cdot 60B_2O_3\).

4. Conclusions

Study of the series of amorphous materials with compositions \(xBi_2O_3 \cdot (40 - x)LiF \cdot 60B_2O_3, x = 0, 5, 10, 15 \text{ and } 20\) reflects following conclusions:

1. XRD analysis, suggests that the samples are amorphous in nature as the XRD spectra of all the samples contain no sharp peak.
2. In FTIR analysis it can be concluded that Bi\(_2\)O\(_3\) plays an important role in modifying the glass network.
The presence of the absorption bands at 901, 1295, and 1370 cm$^{-1}$ attests these modifications which are due to Bi$_2$O$_3$ content and are absent in the sample with $x = 0$. Further, an important conclusion is that with the addition of Bi$_2$O$_3$ in place of some concentration of LiF, there is an almost elimination of an absorption band (685 cm$^{-1}$) and shifting of some absorption band centers (1210 to 1220 cm$^{-1}$ and 1365 to 1370 cm$^{-1}$) from $x = 0$ to $x = 5$, which approves the role of Bi$_2$O$_3$ as a network modifier in the present glass system.

(3) Density and molar volume increase with increase in Bi$_2$O$_3$ content due to replacement of a larger molar mass group (Bi$_2$O$_3$) with a smaller molar mass group (LiF).

(4) Theoretical optical basicity decreases with increase in Bi$_2$O$_3$ content on the cost of LiF content.

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References


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